

PATENT SPECIFICATION

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DRAWINGS ATTACHED.

Inventor:—HYMAN JOSEPH LEVINSTEIN.

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COMPLETE SPECIFICATION.

Process for Producing Lithium Niobate.

We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organised and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to processes for treating or producing lithium niobate crystals, LiNbO_3 (sometimes known as lithium metaniobate).

In recent years, there has been an acceleration of research and development directed toward materials suitable for use in circuit elements, the functions of which depend upon piezoelectricity, ferroelectricity, and various interactions of such properties with forms of electromagnetic and elastic waves. A very few years ago, the group of materials exhibiting any of these properties was dominated by quartz, barium titanate, and a few water-soluble materials which were developed during the wartime quartz shortage. In very recent years, a number of promising inorganic materials, many showing some properties superior to quartz, have emerged. These include the various forms of wurtzite, zinc oxide, cadmium sulphide, and lithium meta-gallate, some of which have electro-mechanical coupling coefficients two or three times that of quartz, and some of which, too, have high electric or elastic values of Q , so permitting their use in proposed devices relying on interactions of piezoelectric properties and wave motion.

During the past years, there has been increased activity directed toward yet another piezoelectric material. This material, lithium niobate, LiNbO_3 , is in many respects the

most exciting of the single crystal piezoelectrics. It is already known that lithium niobate has an electromechanical coupling coefficient of approximately 50 per cent, so manifesting a conversion efficiency in a single crystal material for the first time comparable with the best available materials. Elastic Q values determined from decay time experiments conducted at 500 megacycles per second are of the order of 10^5 , a value comparable to those of yttrium-iron garnet and yttrium-aluminium garnet, both of which are almost isotropic.

Lithium niobate is a water-white material which is transparent over the entire visible spectrum and beyond, including the bandwidth of from 0.4 micron to about 4.5 microns.

These properties have prompted and intensive study directed to the use of lithium niobate in a vast class of devices.

It has been found, for example, that lithium niobate has a birefringence larger than its dispersion for a significant portion of the optical region, so permitting its use as a phase-matchable optical conversion material (harmonic generator, parametric amplifier, etc.). See, for example, Applied Physics Letters, Volume 5, pages 234—236 (1964) and Physical Review Letters, Volume 14, page 973 (1965). Many other device uses involving the above properties are now under study.

The lithium niobate story began to unfold in 1949, Physical Review, Volume 76, page 1886, at which time the authors of that article, Bernd T. Matthias and Joseph P. Remeika, reported certain spontaneously nucleated flux growth crystals. This article contains the first known reference to the possible ferroelectric properties in lithium niobate. The authors here reported the finding of a strong ferroelectric effect in

lithium tantalate and lithium niobate. In a figure the dependence of saturation polarization on temperature is shown for the tantalate. The statement is included that a similar effect may be observed in the niobate, however at higher temperature.

There is a line of references largely based on the Matthias and Remeika paper, supra, which treat the tantalate and niobate as similar in the ferroelectric sense. Nevertheless, from the experimental standpoint, the issue of ferroelectricity in lithium niobate has been a controversial one. While it was determined some time ago that the material is pyroelectric, and while this was recently related to the etching behaviour of the crystal, see *Applied Physics Letters*, Volume 6, page 228 (1965), measurements such as those reported by Matthias and Remeika have never again resulted in the slightest suggestion of a ferroelectric hysteresis. Recently, when it was reported that the ferroelectric Curie point for lithium tantalate was as high as 665°C., (*Fiz. Tverd. Tela*, Volume 6, No. 1, 316—17, 1964) an attempt was made to polarize lithium niobate at this very high temperature. This attempt, too, failed.

Greater impetus was given to the quest for ferroelectricity in lithium niobate. It was only recently discovered that large single crystals of apparent perfection could be grown by crystal pulling, *Journal of the American Ceramic Society*, Volume 48, page 112 (1965), and it was on such crystals that many of the early measurements were made, indicating the device potential indicated above. It was, however, found that the apparent crystalline perfection was marred by the presence of certain imperfections or structures and it was found necessary to minimize or eliminate all such structures from crystalline sections upon which meaningful studies for certain device applications were to be made. Unfortunately, the usable regions in even the best crystals grown by ordinary pulling were of less than one millimeter in maximum dimension. While the properties observed in such selected crystal sections were very promising, and while such sections could, if necessary, have found use in commercially useful devices, it was readily apparent that an improved growth technique was desirable.

While many approaches were tried to minimize or eliminate these structures, and while experiments were carried out simultaneously in more than one direction, an approach that merited particular attention was suggested by the early work of Matthias and Remeika. If, in fact, these structures were due to the presence of ferroelectric domain walls, it was conceivable that an electric field could be utilized to advantage in minimizing or eliminating these domains. Unfortunately, it was well known to those

skilled in this field that the use of almost prohibitively high fields, together with extremely high temperatures, had been totally unavailing in even suggesting the presence of any ferroelectric effect.

According to one aspect of the present invention there is provided a process of treating a lithium niobate crystal, comprising passing an electrical current through at least a portion of a crystal of lithium niobate, while maintaining the said portion at a temperature of at least 1000°C.

According to another aspect of the present invention there is provided a process of producing a lithium niobate crystal by pulling from a melt, wherein an electrical current is passed through the solid-liquid interface between the crystal and the melt during growth.

It was decided to pass a current through a solid-liquid interface region during growth, and it was this technique that ultimately resulted in the growth of a single crystalline material substantially free from the above structures and that established conclusively the fact, for so many years in dispute, that lithium niobate was a ferroelectric material exhibiting an electrical reversibility of polar domains, albeit at a significantly higher temperature than that reported for any other material.

It was discovered that the structure, attributed to the presence of domain walls, may be removed or eliminated by biasing a crystal under specific critical conditions enumerated herein. In one preferred embodiment of this invention, this biasing takes the form of the passage of a current through the solid-liquid interface during crystal pulling. In accordance with this embodiment, absolute control of ferroelectric polarity is achieved. It has been found that reversal in polarity during growth results in a ferroelectric domain wall, created at the time of reversal, separating two regions of opposite ferroelectric polarity. In accordance with a further species of this embodiment, successive bias reversals are used to produce a striated structure of successively alternating polarity.

In accordance with another embodiment of this invention, it has been found that multi-domain structure appearing in lithium niobate crystals of otherwise good quality may be minimized or removed by polarization carried out at a temperature of at least 1000°C.

For a better understanding of the invention reference is made to the accompanying drawing, in which:

Fig. 1 is a front elevational view, partly in section, of apparatus suitable for use in accordance with one embodiment of the invention; and

Fig. 2 is a perspective view of an arrangement found suitable for producing improved

lithium niobate by the polarization of a lithium niobate crystal.

Referring again to Fig. 1, the apparatus depicted is illustrative of the many techniques which may be utilized. This particular apparatus is useful for practicing Czochralski growth and includes a crucible support 1, which, in this instance, is constructed of alumina and so performs the additional function of thermally insulating the inner crucible 2, which is constructed of a precious metal such as platinum and which, in turn, contains melt 3, which is composed of starting ingredients which will yield near-stoichiometric amounts of the constituent elements of the final crystal. In general, it has been found that this melt may deviate from the stoichiometric niobium to lithium ratio of unity by up to approximately 10 atom per cent. The melt may additionally contain any of a large group of additives, generally in amounts of up to 10 atom per cent based on niobium.

While the melt may be prepared by putting the usual starting ingredients, lithium carbonate and niobium oxide, directly into the crucible, the large amounts of carbon dioxide liberated on breakdown of the carbonate are more easily handled in a separate sintering step. Of course, the lithium or niobium may be added in the form of any other compound which will break down to yield the corresponding oxides in the melt.

In general, it has been found that the normally encountered impurities, and in fact, also deliberately added impurities, have little effect on the domain wall-free end product. However, depending on the end use to which the crystal is to be put, it may be desirable to maintain exceedingly close stoichiometry, to exclude to a large extent most or all impurities, or, in fact, as has been noted, to make additions. Where extreme purity and close stoichiometry are particularly desirable, it has been found that this may be accomplished by initially growing crystalline material in accordance with any single crystal growth technique, with or without a field, and to utilize this end product rendered molten as the melt for the controlled procedure to which this embodiment is directed.

Melt 3 is rendered and maintained molten by means of a heating source 4, here illustratively depicted as r.f. heating coils. In keeping with usual good crystal growing practice, it is desirable to maintain the melt at a near constant temperature (in this instance, at a nominal value of about 1300°C.), and to this end the depicted apparatus is provided with a thermocouple sensing means 5. The apparatus is provided, too, with a spindle 6, which is slowly raised and preferably rotated by means not shown, such spindle being provided with chuck 7, hold-

ing seed crystal 8, upon which there has solidified grown crystal 9.

Surprisingly, it has been found that the ability to grow domain wall-free material is substantially insensitive to the impurity content, the presence of imperfections or domain walls, and the orientation of the seed. Of course, good crystal growing practice is always preferred, and the presence of large amounts of impurities and/or significant imperfections will result in a less than optimum end product, at least over the inner portion of the crystal, which may be expected to suffer if only by virtue of the solid-solid diffusion of impurities or the initial perpetuation of imperfections. Except from the theoretical standpoint, there is no forbidden seed orientation. Since the effect of passing current through the interfacial region during growth is one which is asserted solely on the active or *c* axis of the crystal, it follows that such current passage may have no effect on growth proceeding from a seed in which the *c* axis is exactly perpendicular to the growth direction. In practice, however, it is likely that this orientation is never achieved or, alternately, that there is always some imperfection or other condition permitting growth in that direction along which such an influence is felt.

Seed orientations are conveniently expressed in x-ray crystallographic terms, planes being designated as (*hkl*), based on a hexagonal indexing with *a*=5.127Å and *c*=13.856Å, and directions being designated as perpendicular to such planes. In this system, the *c*-axis is perpendicular to (00.1).

The above considerations are solely with a view to bringing about the influence to which this embodiment is directed, i.e., the use of a current or its accompanying field to remove or control domain walls, and in this connection, as has been noted, lithium niobate crystals having successive domains of alternating polarity, have been produced in response to a current of similarly alternating period. From a device standpoint, as is well recognized, the crystallographic orientation of the end product may be quite significant. For example, where the crystal is designed for use in an harmonic generator in which electromagnetic energy is transmitted perpendicular to the *c* axis and where the element is desirably long in the direction of such transmission, it is expedient to start with a grown crystal, also long in that approximate direction. For many piezoelectric device applications, it is desirable to have a crystal having a long dimension approximately corresponding with the *c* axis.

The current technique of this embodiment absolutely controls the polarity (which may be measured pyroelectrically) of the final crystal. In consequence, the polarity of the seed crystal is of no consequence.

Current passage through the solid-liquid inter-facial region in the depicted apparatus is accomplished by means of sliding contact 10 engaging spindle 6 and fixed electrode 11 electrically connected to crucible 2, these 5 biasing the interface, of course via the melt and intervening apparatus elements by means of variable polarity, variable voltage power supply 12. Ammeter 13 is convenient for 10 monitoring the passage of current, particularly where the circuitry is such that there is a wide variation in current magnitude with the length of the grown crystal. This variation, which is generally undesirable, may be 15 minimized by maintaining a circuit impedance in the power supply and associated elements which is large relative to the maximum encountered in the crystal.

The use of an afterheater or other arrangement for minimizing the temperature gradient in the grown crystal, generally of benefit in crystal growth, may enjoy a particular advantage here for maintaining the grown 20 portion at a temperature almost as high as the temperature of the interfacial region, and maintains the resistance of the crystal at a lower value; so keeping the entire circuit resistance more nearly constant.

It is more convenient to consider current 30 passage rather than field value, since it is the former value that is more easily monitored, for example by use of an ammeter such as instrument 13 depicted. Since the interfacial region is in series with the rest 35 of the crystal, and since all the current monitored by the ammeter necessarily passes through this region, this means of control, unlike that of monitoring the electrical field, is independent of the length of grown crystal. In general, the magnitude of the current 40 is not a sensitive parameter. It has been found that currents as low as 0.1 milli-ampere per square centimeter of crystal cross section at the interface are sufficient to 45 bring about substantially domain wall-free material. Currents as large as about 50 ma/cm² have been found to be equally useful, although values substantially in excess of this may be troublesome in that they sometimes 50 bring about excessive Joule heating of the grown crystal. Current values in excess of this quantity are preferably avoided since they may affect growth conditions and, further, since they may bring about localized 55 heating with accompanying thermal and electrical instability. It is to be expected that the effectiveness of current passage decreases as the growth direction departs from pure *c* direction, and this has, in fact, been observed. For growth approaching a direction 60 perpendicular to the *c* axis, a greater minimum value of current, of substantially 10 ma/cm², may be necessary.

Various parameters of concern common 65 to the present embodiment growth tech-

niques and prior art techniques have not been discussed. As in ordinary Czochralski growth, the pulling mechanism, not depicted in the figure, should be 70 such as to permit growth at a rate of four inches per hour or less. Crystal perfection is improved by still slower rates, down to substantially one-tenth inch per hour, at least during bulk growth, at which full diameter has been attained. Rotation of the 75 crystal, or of the crucible relative to the crystal, minimizes the effect of any temperature gradients about the periphery of the crystal and serves also to stir the melt. Where such rotation is utilized, it is desirable 80 that it be at the rate of at least 5 rpm.

The crystal pulling apparatus of Fig. 1 is merely exemplary of one suitable form of apparatus.

Any apparatus permitting seeded growth 85 from a melt permitting biasing of the crystal relative to the melt to permit passage of an electrical current through the solid-liquid interfacial region is suitable. Other such apparatus includes zone melting (most expediently in the form of float zone melting), 90 Bridgman-Stockbarger, providing some means is provided for insulating the melt from the growing crystal, etc., etc.

Fig. 2 is illustrative of a second embodiment of this invention, in accordance with which an already grown crystal is treated by 95 passage of an electrical current so as to minimize or remove domain walls. A lithium niobate crystal under treatment, for the usual 100 purposes to which this material is put, is preferably a single crystal, otherwise of device grade, and, from the same standpoint, as near perfect as available. The presence of imperfections and other flaws, while they 105 may affect the velocity of domain wall movement, do not affect the basic mechanism, so that the preference for device-grade crystals is premised entirely on the use to which these crystals are to be put. 110

Such a crystal, 20, heated, for example, by a resistance-heated tube furnace 21, is shown electrically biased by and suspended out of contact with the furnace by means of electrodes 22 and 23, in turn electrically connected with variable current source 24. The 115 process may be monitored by means of ammeter 25 or voltmeter 26. Temperature control is, in this case, afforded by means of variable power supply 27, to which furnace 21 is connected. Since most refractory materials of which furnaces operating at the requisite temperature may be constructed are substantially conducting at the required temperature levels, it is generally necessary to 120 suspend the crystal as shown or to resort to other means for maintaining it out of contact with a furnace or container wall.

The embodiment represented by Fig. 2 is related to that of Fig. 1 through the dis- 125 130

covery of a Curie point at about 1210°C., and one manner in which this variation may be practised is to drop the temperature of the crystal from a point at or above 1210°C., but below the melt temperature of about 1255°C., through the Curie point while maintaining a current flow through the crystal. Alternatively, treatment or polarization may be accomplished with the crystal held at a constant temperature or range of temperatures below the Curie point, while at the same time passing current through the crystal. For these purposes, it is expedient to operate at a temperature of at least 1000°C., it having been found that treatment at substantially lower temperature requires excessive time. Required treatment time decreases as the Curie point is approached, it having been found that a domain wall-free crystal may be produced in five minutes or less at temperatures of substantially 1200°C. Current densities, as in the practice of the embodiment of Fig. 1, may range from 0.5 ma/cm² up to 50 ma/cm². Still higher current density may result in more rapid treatment, and, while Joule heating results, the disadvantages of excessive current in the embodiment of Fig. 1 are not here serious.

At a temperature of substantially 1200°C., the resistivity of lithium niobate is approximately 140 ohm-cm. In these terms, a current range of 0.5 ma/cm² to 50 ma/cm² is equivalent to a field of 0.7 volt/cm length up to 7 volts/cm. Resistivity increases steeply with dropping temperature and attains a value of about 630 ohm-cm. at a temperature of about 1000°C., this being equivalent to a field range 4½ times that indicated at 1200°C.

The following examples are selected to illustrate some of the conditions which have resulted in substantially domain wall-free lithium niobate crystals.

Example 1

A 100 gram melt was produced by first sintering a mixture of 25 grams of lithium carbonate and 90 grams of niobium oxide at a temperature of about 1000°C. for a period of about ten hours. The sinter was then placed in a platinum crucible such as crucible 2 of the apparatus depicted in Fig. 1. The particular crucible was of 5 cm depth and 5 cm I.D. The contents were melted by use of an r.f. heating coil. Both melting and sintering were carried out in air and it is considered preferable for these purposes that such operations be carried out in an oxygen-containing atmosphere to minimize the likelihood of oxygen deficiencies in the final material. However, as is noted, supposed manifestations of oxygen deficiencies when they occur can be removed by a subsequent treatment described in this example. A seed

crystal, approximately one-half inch in length and one-tenth inch in diameter, of approximately *c* axis orientation (*c* axis perpendicular) was brought into contact with the melt and allowed to remain in such position for approximately ten minutes to bring it into thermal equilibrium. The seed was then biased relative to the melt at such value as to produce current flow of 2 ma. The seed was then withdrawn at a rate of three-quarters inch per hour while being rotated at approximately 100 rpm. Under these conditions, the crystallizing matter quickly attained a diameter of about 1 centimeter which remained substantially constant during drawing. At this diameter, the current density was of the order of 2.5 ma/cm². A total length of approximately 5 centimeters was grown. Growth was terminated by slowly raising the temperature of the melt over a half-hour period so as to taper and finally terminate growth, at which time the grown crystal was removed from the growth apparatus.

The crystal was then annealed in oxygen at a temperature of 1100°C. for a period of ten hours, during which time the pale tanish colour generally considered as characterizing oxygen deficiency bleached out, leaving a water-white crystal.

The crystal was sectioned and polished as described in Applied Physics Letters, Volume 6, page 228 (1965) by mechanical polishing with alumina, first 0.3 micron grit size, followed by 0.05 micron grit size. Optical and microscopic examination revealed freedom from domain walls over a major portion of the crystal.

Example 2

The procedure of Example 1 was followed, however, with the seed crystal oriented at approximately 28 degrees from the *c* axis toward the direction perpendicular to (21.0). In addition, 0.12 gram excess lithium carbonate was present, corresponding to 0.5 atom per cent lithium. The final crystal, of approximately the same dimensions, was found to be essentially domain wall free over a major portion.

Example 3

The procedure of Example 1 was repeated, however, with the seed oriented such that substantially *a* direction growth resulted. The final crystal was again found to be substantially domain wall free.

Example 4

The procedure of Example 2 was repeated, except that 0.5 atom per cent molybdenum oxide based on niobium was added to the melt. The final crystal was found to be substantially domain wall free.

Example 5

The procedure of Example 4 was repeated, but the power supply was regulated so as to result in a current of 10 ma, corresponding with a current density of 12.5 ma/cm² for the finally attained one centimeter crystal. The final product was found to be substantially domain wall free.

Example 6

The procedure of Example 1 was repeated, but the polarity of the current was reversed approximately half way through growth. The final crystal, upon examination, showed the presence of a domain wall approximately half way along its length and was substantially structure free on either side of the wall.

Example 7

The procedure of Example 1 was repeated, however, with the seed crystal oriented at approximately 28 degrees from the *c* axis toward the direction perpendicular to (21.0), and with the addition of 0.25 grams vanadium oxide, V₂O₅, corresponding to 0.4 atom per cent vanadium based on the niobium present. The final crystal was found to be substantially domain wall free over a major portion.

Example 8

A lithium niobate crystal exhibiting structure due to the presence of domain walls was grown by the procedure of Example 2, however, without the passage of current through the interfacial region. The resulting crystal was placed in a tube furnace suspended by platinum electrodes, in turn biased by a power supply. The apparatus utilized is represented by that of Fig. 2. A field of 0.26 volt/cm, or an over-all field of 1.3 volts for the total length of 5 cm processed was maintained as the crystal was dropped in temperature from substantially 1240°C. to substantially 1000°C. over a period of about ten minutes. As has been indicated, this field was equivalent to a current density of about 1.4 ma/cm² with the crystal at a temperature of about 1200°C. The crystal was found to be substantially domain wall free over a major portion.

Example 9

The procedure of Example 8 was repeated, with the said field maintained for a period of 15 minutes, with the crystal held at a constant temperature of about 1200°C. The final crystal was found to be substantially domain wall free.

Example 10

The procedure of Example 9 was repeated, however, utilizing a *c* axis grown

crystal. The final crystal was substantially domain wall free.

Example 11

The procedure of Example 9 was repeated, however, with the crystal maintained at a temperature of about 1110°C. for a period of about 2½ hours and using a 4.0 volt field over the 5 cm length. The final crystal was substantially domain wall free.

Example 12

The procedure of Example 9 was repeated, however, using a crystal growth from a melt containing 0.5 atom per cent molybdenum. The final crystal was found to be substantially domain wall free over a major portion.

Example 13

The procedure of Example 9 was repeated, however, a crystal grown from a melt containing 0.5 atom per cent tungsten was used. The final crystal was found to be substantially domain wall free over a major portion.

The above examples were chosen to show a variation in the more significant parameters of growth primarily with respect to those conditions peculiar to the procedures herein. Accordingly, no examples are included to show permissible variations in growth rate, rotational rate, and other parameters common to prior art techniques.

In the description of the embodiment corresponding with Fig. 1, continual reference has been made to the passage of current through the solid-liquid interfacial region. It has been noted that the Curie temperature for lithium niobate is approximately 1210°C. It is reasonable to assume that a major part of the treatment is effected over that portion of the crystal at or below the Curie point. Since the Curie point is a mere 45 degrees below the melt temperature which obtains at the interface, and since seeded growth ordinarily proceeds with a temperature drop of several hundreds of degrees below the interface, no special precautions need be taken to ensure current passage in a portion of the crystal at or below the Curie temperature.

The invention has been described in terms of a limited number of exemplary embodiments. Certain additional variations such as permissible deviation from stoichiometry and tolerance for or addition of solute materials have been indicated. Certain of the conditions common to the examples were adopted with a view to the particular end use and may not always be necessary. So, for example, the annealing step effective in bleaching the tan coloration considered to identify oxygen deficiency is useful primarily where

the device application is based on light transmission.

WHAT WE CLAIM IS:—

1. Process for treating a lithium niobate crystal, comprising passing an electrical current through at least a portion of a crystal of lithium niobate, while maintaining the said portion at a temperature of at least 1000°C.
2. Process according to claim 1, wherein the current density is at least 0.1 ma/cm².
3. Process of producing a lithium niobate crystal by pulling from a melt, wherein an electrical current is passed through the solid-liquid interface between the crystal and the melt during growth.
4. Process according to claim 3, wherein the current density is maintained at a value of at least 0.5 ma/cm².
5. Process according to claim 4, wherein the direction of current passage is reversed at least once during growth.
6. Process of producing a lithium niobate crystal, substantially as hereinbefore described with reference to any one of examples 1 to 7.
7. Process for treating a lithium niobate crystal, substantially as hereinbefore described with reference to any one of examples 8 to 13.
8. Process of producing a lithium niobate crystal, substantially as hereinbefore described with reference to Fig. 1 of the accompanying drawing.
9. Process for treating a lithium niobate crystal, substantially as hereinbefore described with reference to Fig. 2 of the accompanying drawing.
10. Lithium niobate crystal produced by the process according to any one of the preceding claims.

K. G. JOHNSTON,
Chartered Patent Agent,
5, Mornington Road,
Woodford Green, Essex.
Agent for the Applicants.

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COMPLETE SPECIFICATION

1 SHEET

This drawing is a reproduction of the Original on a reduced scale

